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(54) **Compatible fuel additive concentrates.**

(57) Effective foam control and enhanced additive compatibility is achieved in additive concentrates and liquid fuels containing overbased alkaline earth metal detergents. This is accomplished by utilizing as the antifoam agent a water-soluble polyether-polysiloxane copolymer having a siloxane backbone with organic polyalkylene oxide pendant groups attached to the siloxane backbone via direct silicon-to-carbon bonds. A number of other types of foam inhibitors have been found incapable of achieving these results.

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Foam control is a highly important consideration in the preparation of additive compositions for use in fuels of the middle distillate boiling range, such as gas oils, diesel fuels, gas turbine fuels, burner fuels and the like. If a fuel foams during transfer from one tank to another, it becomes difficult to control flow rates and volumes. Similarly, foaming during the filling of fuel tanks can pose various other problems, such as delivery of inadequate amounts of fuel to the tanks or conversely, overflowing and spillage of fuel at the filling site.

To overcome these foaming problems, a variety of foam inhibitors such as polyacrylates and polysiloxanes have been proposed for use in diesel fuels and additive packages to be used in formulating finished diesel fuels.

When producing certain additive concentrates for use in improving the performance characteristics of middle distillate fuels it has been found necessary to include a fairly high amount of the foam inhibitor in the concentrates to ensure that the finished fuel will have a sufficient level of antifoam additive to effectively suppress or inhibit foam formation in the fuel during operations such as referred to above. In general, amounts of antifoam additive of at least 0.5% by weight in the additive concentrate are required. Indeed, amounts as high as 10% by weight or more of foam inhibitor in the concentrate may be required for effective utilization of some additive concentrates.

It has been discovered that when the additive concentrate contains both a high level of a silicone antifoam agent and an overbased detergent, a serious problem of incompatibility can arise. This problem is manifested in different ways. For one thing, insoluble sediments or particulate matter can be generated in the additive concentrate, especially during storage. Moreover, experimental results indicate that even if the interaction between the overbased detergent and the silicone antifoam agent does not result in visually perceptible amounts of solids, nevertheless this incompatibility can cause a significant loss of antifoam performance in the resultant finished fuel. Concurrent manifestation of both such adverse consequences is also possible.

A need has thus arisen for a way of effectively overcoming this problem of additive incompatibility as between overbased metal detergents and siloxane foam inhibitors especially when the latter are used at relatively high concentrations in additive packages and in resultant fuel compositions.

In fulfilling this need, this invention provides in one of its embodiments an additive concentrate which comprises as components thereof (i) at least one overbased alkali or alkaline earth metal-containing detergent and (ii) a water-soluble polyether-polysiloxane copolymer having a siloxane backbone with organic poly(alkylene oxide) pendant groups attached to the siloxane backbone via direct silicon-to-carbon bonds. These copolymers also have hydrocarbyl pendant groups, preferably methyl groups, attached to the siloxane backbone via direct silicon-to-carbon bonds. The weight ratio of (i) to (ii) on an active ingredient basis is normally in the range of about 0.25 to about 250 parts by weight of (i) per part by weight of (ii).

Another embodiment involves including in the above additive concentrate as a component thereof (iii) at least one hydrocarbon-soluble ashless dispersant, the weight ratio of (iii) to (ii) on an active ingredient basis being in the range of about 0.25 to about 300 parts by weight of (iii) per part by weight of (ii).

Preferred compositions of this invention are any of those described above wherein the concentrate further comprises as a component thereof (iv) at least one hydrocarbon-soluble cyclopentadienyl manganese tricarbonyl compound, the weight ratio of (iv) to (ii) on an active ingredient basis being in the range of about 0.07 to about 25 parts by weight of (iv) per part by weight of (ii).

Other components which may be, and preferably are, included in any of the foregoing concentrates are a liquid hydrocarbon diluent (especially a liquid highly aromatic hydrocarbon diluent) or a liquid alcohol diluent or a demulsifying agent or a corrosion inhibitor, or any mixture of any two or more of the foregoing.

Still other embodiments include liquid fuel compositions, such as fuels boiling in the middle distillate boiling range, containing the components in accordance with any of the foregoing additive concentrates.

The above and other embodiments and advantages of this invention will become still further apparent from the ensuing description and appended claims.

COMPONENT (i)

The metal-containing detergents are exemplified by oil-soluble overbased salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulfurized alkylphenols, (6) organic phosphorus acids characterised by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of the above acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The term "overbased" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the overbased salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralising agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide, carbonating the mixture in the presence of a promoter, and filtering the resulting mass. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine, and dodecylamine. A particularly effective method for preparing the overbased salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralising agent and at least one suitable promoter, and carbonating the mixture at an elevated temperature such as 60°-200°C.

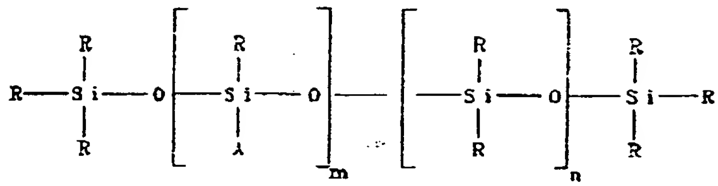
Examples of suitable overbased metal-containing phenate detergents include, but are not limited to, such substances as overbased lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized lithium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility. The foregoing overbased metal detergents are often referred to as "overbased" phenates or "overbased sulfurized phenates". Examples of overbased sulfonates include overbased lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility. Overbased salicylate detergents are exemplified by lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility. Also suitable though less preferred are (a) the overbased lithium, sodium, potassium, calcium and magnesium salts of hydrolysed phospho-sulfurized olefins having 10 to 2000 carbon atoms or of hydrolysed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms; and (b) the overbased lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids, this latter category often being referred to as "overbased carboxylates". Other similar overbased alkali and alkaline earth metal salts of oil-soluble organic acids are suitable, such as the overbased aliphatic sulfonate salts, often referred to as "petroleum sulfonates", such as the overbased lithium, sodium, potassium, calcium and magnesium petroleum sulfonates. Mixtures of salts of two or more different overbased alkali and/or alkaline earth metals can be used. Likewise, salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more overbased calcium phenates with one or more overbased calcium sulfonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. Likewise, while barium salts are effective, the status of barium as a heavy metal under a toxicological cloud renders barium salts less preferred for present-day usage. Preferred are calcium and magnesium sulfonates, sulfurized phenates and salicylates having a total base number (TBN) per ASTM D 2896-88 of at least 200, and preferably above 250.

COMPONENT (ii)

An important aspect of this invention is that the foam inhibitor used is of a makeup and type that does not exhibit the serious incompatibility with overbased metal detergents as is exhibited by a wide variety of siloxane-type foam inhibitors.

As noted above, this invention utilizes certain water-soluble polyether-polysiloxane copolymers having poly(alkylene oxide) pendant groups attached to a siloxane backbone via carbon-to-silicon bonds. By "water-soluble" is meant that the copolymer is sufficiently soluble in water such that a clear water solution containing at least 15 weight percent of the copolymer can be formed at 25°C. Preferably, the polysiloxane backbone of the copolymer is also partially substituted by short chain hydrocarbyl groups such as methyl, ethyl or vinyl, most preferably methyl. Likewise, the preferred poly(alkylene oxide) pendant groups in the copolymer are poly(ethyleneoxy) groups or poly-co(ethyleneoxypropyleneoxy) groups which latter may have the $-C_2H_4O-$ and $-C_3H_6O-$ groups arranged randomly or in block sequences. In the usual situations, the propyleneoxy groups are branched chain groups in which an ethyleneoxy group is substituted with a pendant methyl group.

One preferred type of copolymers are the water-soluble copolymers of the formula



where R is a short chain group (e.g., methyl, ethyl, propyl, vinyl), A is a poly(alkylene oxide) group in which the alkylene moieties are ethylene and/or propylene, and m and n are numbers such that the copolymer is water-soluble as defined above. Most preferably, the poly(alkylene oxide) groups have a terminal hydroxyl groups. An example is where A is the group:

$$-(CH_2)_3-O-(C_2H_4O)_x\,(C_3H_6O)_y\,H$$

Most preferably, R is methyl, and the polyalkylene oxide groups contain at least 60 weight percent ethyleneoxy moieties with the balance, if any, being propyleneoxy moieties. Copolymers in which the siloxane content falls in the range of about 10 to about 60 weight percent may be found suitable.

Especially preferred are liquid polyether-polydimethylsiloxane copolymer having about 75 weight percent ethyleneoxy moieties and about 25 weight percent propyleneoxy moieties in the polyether portion of the copolymer, which polyether portions each terminate with a hydroxyl group. Products of this type in which the siloxane content is in the range of about 25-35 weight percent are highly desirable.

At present, the most preferred copolymer is TEGOPREN® 5851 silicone surfactant available from T.H. GOLDSCHMIDT AG, Essen, Germany. This product is described as a diesel antifoam additive which is a polyether polymethylsiloxane copolymer having a siloxane content of about 30%, an ethyleneoxy/propyleneoxy content of 75:25, a terminal hydroxyl group on the polyether groups, a refractive index at 20°C of 1.450 ± 0.005 and a cloud point in water at 1% concentration of 64 ± 3 °C. This product has a water solubility of well above 15 weight percent at 25°C.

COMPONENT (iii)

Among the preferred embodiments of this invention is inclusion in the compositions of at least one hydrocarbon-soluble ashless dispersant in proportions such as described above. These ashless dispersants comprise long chain succinimides, long chain succinic esters, long chain succinic ester-amides, long chain polyamines and long chain Mannich bases. The long chain of these detergent-dispersants contains an average of at least 20 carbon atoms, e.g., an average of 30 to 200 or more carbon atoms. Such long chain substituents are usually derived from polyolefin oligomers or polymers of suitable number average molecular weights such as about 800, 950, 1200, 1350, 1500, 1700, 2100 or 2300 which in turn are formed by polymerization or copolymerization of olefin monomers such as propylene, butylenes, isobutylene, amylenes, mixtures of ethylene and propylene, and the like.

Methods of for the manufacture of such dispersant-detergents suitable for use, inter alia, as additives for fuel compositions are well known and reported in the literature. Thus, typical succinimides that can be used are described in published PCT Patent Application WO 93/06194 and published European Patent Application, Publication No. 0441014 (August 14, 1991). For exemplary disclosures of succinic esters or succinic ester-amides, one may refer for example to U.S. Pat. Nos. 3,184,474; 3,331,776; 3,381,022; 3,522,179; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540. Long chain polyamine dispersant-detergents are described for example in U.S. Pat. Nos. 3,275,554; 3,394,576; 3,438,757; 3,454,555; 3,565,804; 3,671,511; 3,821,302; and European Patent Publication No. 382,405. Suitable fuel-soluble Mannich base detergent-dispersants which can be used are disclosed for example in U.S. Patent Nos. 3,948,619; 3,994,698; and especially 4,231,759.

One preferred group of dispersant-detergents for use in this invention are succinimides formed by reaction of a polyisobutenyl succinic anhydride and a polyamine, especially an ethylene polyamine having an average of 2 to 6 nitrogen atoms per molecule such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and N-[2-hydroxyethyl)-ethylene diamine. In these dispersants, the polyisobutenyl group preferably has a GPC number average molecular weight in the range of 750 to 2300, more preferably 800 to 1350.

Also preferred are the Mannich base dispersants formed by reaction of (i) an alkylphenol in which the alkyl group is derived from a olefin polymer that has a number average molecular weight in the range of 750 to 2300, preferably 800 to 1350 and most preferably 800 to 1100, (ii) polyalkylene polyamine and (iii) formaldehyde or a formaldehyde precursor. Most preferably, the alkyl group of the alkylphenol is derived from polypropene hav-

ing a number average molecular weight in the range of 800 to 1100, and the polyalkylene polyamine is diethylene triamine. Other useful dispersants are referred to, for example, in EP 476,196 B1.

COMPONENT (iv)

Materials which can be, and preferably are, included in the compositions of this invention are cyclopentadienyl manganese tricarbonyl compounds. Such compounds, when present in the finished fuels, contribute materially to reduction of exhaust emissions, particularly emission of particulates and smoke. In addition, use of the cyclopentadienyl manganese tricarbonyl compounds in the compositions of this invention results in further improvements in induction system cleanliness, particularly cleanliness of inlet valves. Cyclopentadienyl manganese tricarbonyl compounds which can be used in the practice of this invention include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds. Preferred are the cyclopentadienyl manganese tricarbonyls which are liquid at room temperature such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl, etc. Preparation of such compounds is described in the literature, for example, U.S 2,818,417.

Although less preferred, other fuel-soluble or fuel-dispersible manganese compounds may be included in the compositions of this invention. These compounds are illustrated by manganese oleate, manganese naphthenates, manganese octylacetoacetate and manganese ethylene diamine tetracetate.

OTHER COMPONENTS

Various other suitable components may be included in the compositions of this invention. Typical materials that may be so included are identified below.

Liquid hydrocarbon diluents.

Various liquid hydrocarbons, such as those boiling in the middle distillate boiling range, can be used as diluents. For best results, hydrocarbons enriched in cycloaliphatic or aromatic hydrocarbons are preferred. Aromatic hydrocarbons such as toluene, xylene, and mixtures such as aromatic naphthas boiling in the range of 160 to 300°C and having a viscosity in the range of 1.4 to 3.0 cSt at 25°C are highly suitable materials.

Liquid alcohol diluents.

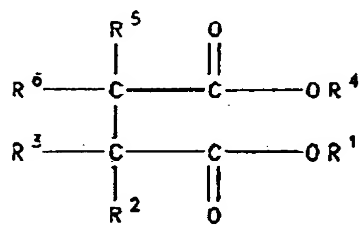
Any alcohol that is fuel-soluble and liquid at ambient room temperatures can be used as diluents. Preferred are liquid fuel-soluble alkanols having in the range of 5 to 13 carbon atoms per molecule. Most preferred are liquid branched chain primary alkanols having 7 to 13 carbon atoms in the molecule or blends of alcohols containing a major amount of one or more such branched chain primary alkanols.

Demulsifying agents.

A wide variety of demulsifiers are available for use in the practice of this invention, including, for example, polyoxyalkylene glycols, oxyalkylated phenolic resins, and like materials. Particularly preferred are mixtures of polyoxyalkylene glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Petrolite Corporation under the TOLAD trademark. One such proprietary product, identified as TOLAD 9310, is understood to be a mixture of these components dissolved in a solvent composed of heavy aromatic naphtha and isopropanol. This product has been found efficacious for use in the compositions of this invention. However, other known demulsifiers can be used such as TOLAD 286K and OFRIC D5021 available commercially from Baker Performance Chemical (a division of Baker Hughes Limited).

Corrosion inhibitors.

Here again, a variety of materials are available for use as corrosion inhibitors in the practice of this invention. Thus, use can be made of dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humko Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of corrosion inhibitor for use in the practice of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, dodecenylsuccinic acid, dodecenylsuccinic anhydride, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, and hexadecenylsuccinic anhydride. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Still another group of suitable materials is the succinic acids or derivatives thereof represented by the formula:



wherein each of R^2, R^3, R^5 and R^6 is, independently, a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and wherein each of R^1 and R^4 is, independently, a hydrogen atom, a hydrocarbyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms.

The groups R^1, R^2, R^3, R^4, R^5, and R^6 when in the form of hydrocarbyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R^1, R^2, R^3, R^4 and R^5 are hydrogen or the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R^1, R^2, R^3, R^4, and R^5 are hydrogen atoms. R^6 when in the form of a hydrocarbyl group is preferably a straight-chain or branched-chain saturated hydrocarbon radical.

Most preferred of this type of corrosion inhibitor is a tetraalkenyl succinic acid of the above formula wherein R^1, R^2, R^3, R^4 and R^5 are hydrogen and R^6 is a tetrapropenyl group.

Preferred corrosion inhibitors for use in this invention are low molecular weight succinimide/amide of polyalkylene polyamine. One commercially-available material of this type is HITEC® 536 corrosion inhibitor (Ethyl Petroleum Additives Limited). Also preferred are neutral corrosion inhibitors some of which are available under the HiTEC trademark.

Carrier fluids.

There are various types of material useful as agents to assist in transporting additives of low volatility into the engine. These include mineral oils, poly-α-olefin oligomer fluids (hydrogenated or unhydrogenated), polyoxyalkylene glycols, polyoxyalkylene glycol ethers, polyoxyalkylated phenols, long chain ester fluids, and similar materials. Mixtures of two or more different carrier fluids can also be used. Typically the carrier fluids have viscosities of up to 10 cSt at 100°C.

Antioxidants.

Of various materials that can be used for this purpose, phenolic antioxidants are generally among the more preferred materials. These include mononuclear monohydric phenols and alkylene bridged alkylphenols. Preferably, these fuel-soluble phenolic antioxidants have from 10 to 30 carbon atoms per molecule and are sterically hindered. Suitable materials include 2-tert-butylphenol, 2,6-di-tert-butylphenol,2,4,6-tri-tert-butylphenol,4-methyl-2,6-di-tert-butylphenol,2,4-dimethyl-6-tert-butylphenol, N-(3,5-di-tert-butyl-4-hydroxybenzyl)-N.N-dimethylamine, 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol),4,4'-methylenebis(2,6-di-tert-butylphenol), and mixed sterically-hindered methylene bridged polyalkylphenols.

Metal deactivators.

Generally speaking, metal deactivators fall into two broad categories. One category comprises the passivators which are considered to react with the metal surface and thereby passivate the surface. The other category comprises the chelators, i.e., substances which have the capability of reacting or complexing with dissolved metal and/or metal ions. An example of the passivator type is the thiadiazoles such as HITEC 314 additive (Ethyl Petroleum Additives, Ltd.; Ethyl Petroleum Additives, Inc.). Examples of the chelator type of metal deactivators include 8-hydroxyquinoline, ethylene diamine tetracarboxylic acid, β-diketones such as acetylacetone, β-ketoesters such as octyl acetoacetate, and the like. The preferred metal deactivators which are generally regarded as chelators, are Schiff bases, such as N,N'-disalicylidene-1,2-ethanediamine, N,N'-disalicylidene-1,2-propanediamine, N,N'-disalicylidene-1,2-cyclohexanediamine, and N,N"-disalicylidene-N'-methyldipropylenetriamine. Thus a wide variety of known metal deactivators are available for use as component f) in the embodiments of this invention which involve use of a metal deactivator.

A particular advantage associated with the use of the metal deactivators, especially of the Schiff base chelator type, is their ability to overcome instability caused in certain hydrocarbonaceous base fuels by the presence of typical manganese carbonyl compounds such as the cyclopentadienyl manganese tricarbonyls in combination with typical metal detergents. The most preferred metal deactivators of this type are N,N'-disalicylidene-1,2-alkanediamines and N,N'-disalicylidene-1,2-cycloalkanediamines, especially N,N'-disalicylidene-1,2-propanediamine. Mixtures of metal deactivators can be used.

Cold flow improvers.

Materials of this type are typified by fuel-soluble polymers, certain types of Friedel-Crafts condensation products, and various proprietary additive mixtures. Among suitable materials are those disclosed in GB 1,436,793; GB 1,486,077; EP 003,489; EP 021,607; EP 155,171; EP 155,807; EP 282,342; EP 283,293; EP 308,176; EP 406,684; EP 465,042; US 3,883,318; US 3,910,776; US 3,955,940; US 3,961,915; US 4,019,878; US 4,142,866; US 4,184,851; US 4,251,232; US 4,512,775; US 4,553,980; US 4,639,256; and US 4,846,847.

Wax antideposition or wax inhibitor additives.

Some additives or additive mixtures have the property of either preventing deposition of wax and/or inhibiting the formation of wax. Such additive compositions can also be used in the fuels of this invention. Illustrative materials are described for example in EP 153,176.

FUELS

In principle, the advantages of this invention may be achieved in any liquid fuel derived from petroleum, biomass, coal, shale and/or tar sands. In most instances, at least under present circumstances, the base fuels will be derived primarily, if not exclusively, from petroleum.

The invention is thus applicable to such fuels as kerosene, jet fuel, aviation fuel, diesel fuel, home heating oil, light cycle oil, heavy cycle oil, light gas oil, heavy gas oil, bunker fuels, residual fuel oils, ultra heavy fuel oils, and in general, any liquid (or flowable) product suitable for combustion either in an engine (e.g., diesel fuel, gas turbine fuels, etc.) or in a burner apparatus (e.g., gas oils, inland heavy fuel oil, residual fuel oils, visbreaker fuel oils, home heating oils, etc.). Other suitable fuels may include liquid fuels derived from biomass, such as vegetable oils (e.g., rapeseed oil, jojoba oil, cottonseed oil, etc.); or refuse-derived liquid fuels such as fuels derived from municipal and/or industrial wastes; or waste oils and/or liquid waste biomass and its derivatives; or mixtures of any of the foregoing substances.

In many cases, specifications exist for various fuels or grades thereof, and in any event the nature and character of such fuels are well-known and reported in the literature.

CONCENTRATIONS

In general, the components of the additive compositions are employed in the fuels in minor amounts sufficient to improve the combustion characteristics and properties of the base fuel in which they are employed. The amounts will thus vary in accordance with such factors as base fuel type and service conditions for which the finished fuel is intended. However, generally speaking, the following concentrations (ppm) of the components (active ingredients) in the base fuels are illustrative:

	General Range	Preferred Range	Particularly Preferred Range
Component i)	10 - 250	15 - 150	40 - 110
Component ii)	1 - 40	5 - 25	8 - 20

In the case of fuels additionally containing one or more of components iii) and iv), the following concentrations (ppm) of active ingredients are typical:

	General Range	Preferred Range	Particularly Preferred Range
Component iii)	10 - 300	20 - 200	50 - 90
Component iv)	3 - 25	5 - 20	9 - 15

It will be appreciated that the individual components i) and ii), and also iii) and/or iv) (if used), can be separately blended into the fuel or can be blended therein in various subcombinations, if desired. Ordinarily, the particular sequence of such blending steps is not critical. Moreover, such components can be blended in the form of a solution in a diluent. It is preferable, however, to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

The additive concentrates of this invention will contain components i) and ii), and optionally, but preferably, one or more of components iii) and iv), in amounts proportioned to yield fuel blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 90% by weight of one or more diluents or solvents are frequently used.

EXAMPLES

The results of an extensive series of experiments illustrate the practice of and advantages made possible by this invention. Additive concentrates for testing were prepared by blending a variety of known commercially-available antifoam agents with an additive package containing a substantial proportion of overbased calcium alkylbenzene sulfonate. For ease of reference these antifoam agents are identified hereinafter as follows:

Antifoam Agent	Description
A	Water-soluble polyether-polysiloxane copolymer having a siloxane backbone with organic polyalkylene oxide pendant groups and methyl groups attached to the siloxane backbone via direct silicon to carbon bonds - Tegopren 5851 (TH. GOLDSCHMIDT AG)
B	Polyether-polysiloxane copolymer that formed a cloudy white dispersion when an attempt was made to form at 25°C a water solution containing 10% by weight thereof - Q2 2600 (Dow Corning Limited)
C	Polyether-polysiloxane copolymer that formed a cloudy mixture that separated into two phases when an attempt was made to form at 25°C a water solution containing 10% by weight thereof - V 4109 (Hoechst AG); S911 (Wacker Chemie GmbH)
D	40% Polyacrylate foam inhibitor in 60% kerosine - HiTEC® 2030 additive (Ethyl Petroleum Additives Limited)
E	20% Linear poly(dimethylsiloxane) with a viscosity of 12,500 cSt at 25°C in 80% kerosine wherein the polysiloxane is DC 200 (Dow Corning Limited)

Antifoam agent A represents a material that meets the requirements for use in the practice of this invention whereas the other antifoam agents do not comply with the requirements of this invention.

The antifoam agent-free additive package was composed of 33% of a commercial overbased calcium alkylbenzene sulfonate which has a nominal TBN of 300 (HiTEC® 611 additive; Ethyl Petroleum Additives Limited), 4.5% of a 62% solution of methylcyclopentadienyl manganese tricarbonyl in light petroleum naphtha,

13.12% of a polyisobutenyl succinimide ashless dispersant (HiTEC® 9645 additive; Ethyl Petroleum Additives Limited), 0.95% of rust inhibitor (HiTEC® 536 additive; Ethyl Petroleum Additives Limited), 1.0% of demulsifying agent (OFRIC D5021; Baker Performance Chemical), and 47.43% of isodecanol.

The base fuel used in all tests was a commercially-available additive-free diesel fuel having a sulfur content of about 0.3% by weight. This fuel had the following distillation profile when subjected to the IP 123 test procedure:

Initial boiling point	177.9°C
10% distillation point	236.4°C
50% distillation point	278.9°C
90% distillation point	355.9°C

The fuel had an aromatics content of 29.53% as determined by the IP 391 procedure.

In one group of tests, measured quantities of different antifoam agents were added to separate portions of the antifoam agent-free additive concentrate and the resultant additive concentrates were then promptly blended into the base fuel to produce fuel compositions which in each case contained an amount of the additive concentrate equivalent to 400 parts per million by volume (ppm v/v) of the antifoam agent-free additive package along with a specified amount of the antifoam agent which had been included in the package. The respective fuels were then promptly shaken under controlled conditions, and in each instance the time needed for the foam to dissipate was measured. (The procedure involved use of graduated glass cylinders, as employed in ASTM D 1094, that had been cleaned in chromic acid for a minimum of one hour, rinsed with water followed by acetone and then dried. The cylinders were filled to the 80 mL mark with fuel. They were then stoppered and shaken for 2 minutes at 2-3 strokes per minute, each stroke being 13 to 25 cm long and in a vertical plane. The shaken cylinders were then placed on a bench and the time for the appearance of a clear foam-free liquid (i.e., the foam dissipation time) was recorded.) A control run (Run No. 1) was also conducted in which the base fuel contained 400 ppm v/v of the additive package but no antifoam agent. Under these same test conditions the additive-free base fuel required 24.5 seconds for foam dissipation. The additive systems used and the results obtained are summarized in Table 1.

Table 1

- Foam Inhibition Tests			
Run No.	Antifoam Agent	Antifoam Agent Concentration, ppm v/v	Foam Dissipation, Time, seconds
1	None	None	22.5
2	B	4	650
3	C	1	29.5
4	C	5	101
5	C	10	329
6	D	1	37
7	D	5	31
8	D	10	39
9	A	2.4	15
10	A	3	5.5
11	A	4	9
12	A	6	5

The data in Table 1 show that as compared to the comparative antifoam agent-free composition only one of

the antifoam agents had any beneficial effect at practical dosage levels in reducing foam formation in the diesel fuel compositions tested. This antifoam agent was antifoam agent A. Antifoam agent E could not be evaluated in this test because when added to the antifoam agent-free package, a gel was formed.

Further tests demonstrating the effectiveness of antifoam agent A were also carried out. These tests were performed as above except that fuels made from freshly prepared additive concentrates containing an antifoam agent were tested and then the concentrates were allowed to age under ambient room temperature conditions before again blending them into additional portions of the base fuel for foam inhibition testing. The test results are summarized in Table 2. In these tests the concentrate dosage levels were at 412 ppm v/v of which 12 ppm consisted of the antifoam agent.

Table 2

- Effect of Aging Additive Concentrates			
Run No.	Antifoam Agent	Aging Conditions, if any	Foam Dissipation Time, seconds
13	A	None; Fuel was tested promptly after unaged concentrate was blended therein	None - no foam formed
14	A	Fuel was tested promptly after blending therein concentrate that had aged for about 1 day	None - no foam formed
15	A	Fuel was tested promptly after blending therein concentrate that had aged for about 39 days	None - no foam formed

Runs 13-15 show that the concentrates and fuels of this invention retained their effectiveness in foam suppression for as long as 39 days.

Another group of tests has shown that the incompatibility of antifoam agents with the additive concentrate is largely due to the presence of an overbased alkaline earth metal detergent in the additive concentrate. In this group, a series of antifoam agent-free additive concentrates was made up from the components described above but in which the components were sequentially omitted. Then an antifoam agent that previously had exhibited incompatibility with the full concentrate (antifoam agent B) was blended with each such concentrate at a concentration level as shown in Table 3. These concentrates were then blended into the base fuel in amounts (v/v) shown in Table 3. In addition, a reference run (Run 1) was made in which the same amount of the same antifoam agent was added to the complete package. The presence or absence of incompatibility was indicated by the results of duplicate foam tests conducted as above -- the longer the time the foam dissipation the greater the incompatibility. Table 3 summarizes the materials used and the results. In Table 3 the numerical values for the components represent the relative proportions of the components, the treat rates are expressed in terms of ppm v/v, the times are expressed in terms of minutes and seconds in duplicate runs and represent the times required for the foam to dissipate, and the above components of the concentrate are identified as follows:

OCAS = overbased calcium alkylbenzene sulfonate
MCMT = methylcyclopentadienyl manganese tricarbonyl in light petroleum naphtha
PIBS = polyisobutenyl succinimide ashless dispersant
RINH = rust inhibitor
DMUL = demulsifying agent
ISOD = isodecanol
AFAB = antifoam agent B

Table 3 - Incompatibility Evaluations

Run No.	OCAS	MCMT	PIBS	RINH	DMUL	ISOD	AFAB	Treat Rate	Time
1	.33	.045	.1312	.0095	.01	.4743	.03	412	29:17 30:36
2	None	.045	.1312	.0095	.01	.4743	.03	280	0 0
3	.33	None	.1312	.0095	.01	.4743	.03	394	1:48 1:50
4	.33	.045	None	.0095	.01	.4743	.03	359.5	47:13 58:00
5	.33	.045	.1312	None	.01	.4743	.03	408.2	8:30 11:36
6	.33	.045	.1312	.0095	None	.4743	.03	408	41:56 44:19
7	.33	.045	.1312	.0095	.01	None	.03	222.3	--*

* Product too viscous to prepare

The results in Table 3 indicate that the principal incompatibility arises from some type of adverse interaction between the overbased metal detergent and the antifoam agent. Thus, the product used in Run 2 which was devoid of overbased metal detergent exhibited no incompatibility as the foam inhibitor was completely effective in that mixture. On the other hand, in each of the other runs tested (Runs 3-6); the presence of the overbased metal detergent caused a significant loss of foam suppression.

Based upon available information concerning structure and properties provided by the manufacturer, the following commercial foam inhibitors are also deemed suitable for use in the practice of this invention: SILWET® L-7604, L-7607, L-7600, L-7605, and L-7200 Surfactants (Union Carbide Corporation).

Claims

1. An additive concentrate which comprises as components thereof (i) at least one overbased alkali or alkaline earth metal-containing detergent and (ii) a water-soluble polyether-polysiloxane copolymer having a siloxane backbone with hydrocarbyl groups and organic polyalkylene oxide pendant groups attached to the siloxane backbone via direct silicon-to-carbon bonds, the weight ratio of (i) to (ii) on an active ingredient basis being in the range of about 0.25 to about 250 parts by weight of (i) per part by weight of (ii).

2. A concentrate in accordance with Claim 1 further comprising as a component thereof (iii) at least one hydrocarbon-soluble ashless dispersant, the weight ratio of (iii) to (ii) on an active ingredient basis being in the range of about 0.25 to about 300 parts by weight of (iii) per part by weight of (ii).

3. A concentrate in accordance with Claim 1 or Claim 2 further comprising as a component thereof (iv) at least one hydrocarbon-soluble cyclopentadienyl manganese tricarbonyl compound, the weight ratio of (iv) to (ii) on an active ingredient basis being in the range of about 0.07 to about 25 parts by weight of (iv) per part by weight of (ii).

4. A concentrate in accordance with any of the preceding claims further comprising as component(s) thereof a hydrocarbon diluent or an alcohol diluent, or a mixture thereof.

5. A concentrate in accordance with any of the preceding claims further comprising as component(s) thereof a demulsifying agent or a corrosion inhibitor, or a mixture thereof.

6. A concentrate in accordance with any of the preceding claims wherein (i) comprises at least one alkali or alkaline earth metal sulfonate having a total base number of at least 200.

7. A concentrate in accordance with Claim 6 wherein the sulfonate is a calcium alkylbenzene sulfonate having a total base number above 250.

8. A concentrate in accordance with any of the preceding claims wherein (ii) is a polyether-polydimethylsiloxane copolymer in which the polyalkylene oxide pendant groups are composed of ethylene oxide and propylene oxide groups in a weight ratio of about 75% -(C_2H_4O)- groups and about 25% -(C_3H_6O)- groups and in which said copolymer has a siloxane content of about 30% by weight.

9. A liquid fuel containing components in accordance with any of Claims 1-8.

10. A fuel in accordance with Claim 9 wherein said fuel is a fuel boiling in the middle distillate fuel boiling range.

11. A fuel in accordance with Claim 9 or 10 wherein the fuel additionally contains an antioxidant.

12. A fuel in accordance with any of Claims 9-11 wherein the fuel additionally contains a cold flow improver.

13. A fuel in accordance with any of Claims 9-12 wherein the fuel is a diesel fuel.

14. A fuel in accordance with Claim 13 wherein the fuel additionally contains a cetane improver.

15. A fuel in accordance with Claim 14 wherein the cetane improver is an organic nitrate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 3035

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,Y	EP-A-0 476 196 (ETHYL PETROLEUM ADDITIVES) * page 11, line 16 - line 20; example 1 *	1-15	C10L1/14
Y	WO-A-93 08244 (EXXON) * page 22 - page 24 *	1-15	
P,Y	WO-A-95 03377 (EXXON) * page 4 * * page 7 *	1-15	
Y	FR-A-2 579 481 (DOW CORNING) * the whole document *	1-15	
A	US-A-4 460 380 (REHRER) * column 7, line 44 - line 47 *	1,8	
A	EP-A-0 529 161 (ETHYL PETROLEUM ADDITIVES) * the whole document *	1-15	
A	EP-A-0 001 318 (EXXON) * page 4, line 121 - line 140 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US-A-4 428 850 (ZOLESKI ET AL.) * column 4, line 57 - line 61 *	1	C10L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 August 1995	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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